Heat Treatment and Surface Hardening (Part-II)

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Lecture - 03

Recap - III

Hello everyone. Let us start our third lecture. In first two lectures, we have seen what we have done in phase-1; and it was a kind of a very brief review. And we have seen that we started mainly with a single component system, and we have touched binary system. And we have realized that the crux of heat treatment which is nothing but time and temperature plus if needed deformation will be decided by a fundamental diagram which is called TTT diagram which is based on overall transformation kinetics which is called a Johnson Mehl Avrami Kolmogorov equation.

And actually we ended there in last phase, however this TTT diagram can also be converted into CCT diagram which is continuous cooling transformation diagram which is more of a practical sense because most of the heat treatments are carried out while doing continuous cooling from a transformation temperature. So, those cases we have to take care of TTT diagram. And the cases where we try to get the transformation and required phases and properties by isothermal treatment by quenching the material from the transformation point to the temperature, we would like to hold the material for different durations that time we do take care of do take help from TTT diagram.

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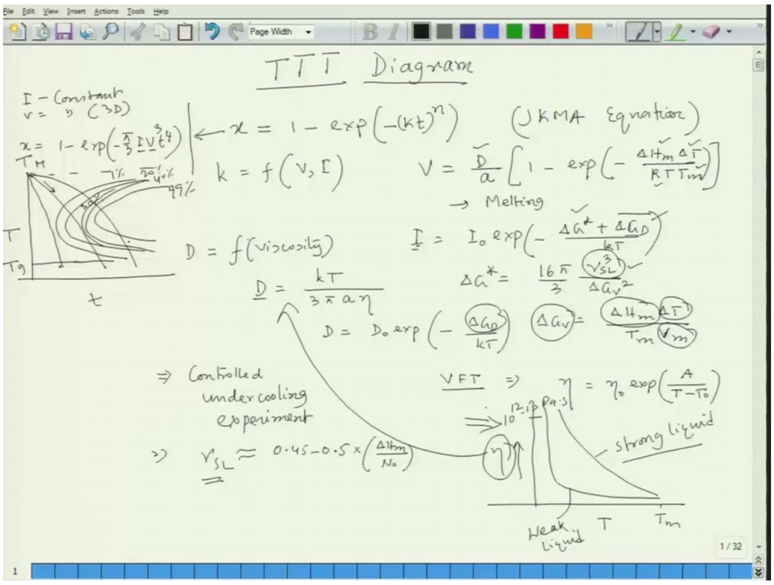

TTT Diagram

I – Constant
v = " (3D)

$x = 1 - \exp\left(-\frac{\pi}{3} I v^3 t^4\right)$ ← $x = 1 - \exp\left(-(kt)^n\right)$ (JKMA Equation)

$k = f(v, I)$

$V = \frac{D}{a}\left[1 - \exp\left(-\frac{\Delta H_m \Delta T}{R T T_m}\right)\right]$

→ Melting

$I = I_0 \exp\left(-\frac{\Delta G^* + \Delta G_D}{kT}\right)$

$\Delta G^* = \frac{16\pi}{3}\frac{\gamma_{SL}^3}{\Delta G_v^2}$

$\Delta G_v = \frac{\Delta H_m \Delta T}{T_m V_m}$

$D = f(\text{viscosity})$

$D = \frac{kT}{3\pi a \eta}$

$D = D_0 \exp\left(-\frac{\Delta G_D}{kT}\right)$

⇒ Controlled undercooling experiment

⇒ $\gamma_{SL} \approx 0.45 - 0.5 \times \left(\frac{\Delta H_m}{N_0}\right)$

VFT ⇒ $\eta = \eta_0 \exp\left(\frac{A}{T - T_0}\right)$

So, it is basically mainly the TTT diagram, which is important for heat treatment. And actually this TTT diagram tells you that what temperature and what time you would like to employ for getting some sort of changes in your material, which is desired by you. And we have also seen that this TTT diagram can be drawn on the basis of one expression which is termed in this fashion which is nothing but JKMA equation. Now, there we have seen that k is the function of growth rate which is velocity of product front growing into parent material; and I, which is nucleation rate.

And our sole interest was to measure V and I in case of single component system, we saw that V can be written in this form and this especially for melting. and I can be written in this form del G D where del G D is basically this term is basically coming from the activation energy for atomic jump from one site to another site. And del G star can be written as square where gamma is solid liquid interfacial energy for in case of solidification; and del G V can be measured from a simple equation which is nothing but del H m del T T m V m, which is molar volume of that metal, and this is also related to melting. And interestingly this del H m is nothing but the melting enthalpy of that material at T m.

Now, in the previous phase we try to measure this V because in case of melting at least we know del H m, we know the under cooling where the transformation is taking place we know melting temperature. R is universal gas constant; d is the diffusivity. And in case of melting this diffusivity can be related to viscosity. And if you consider Stokes Saanson equation, we can relate viscosity with D in this form, where a is the lattice parameter, k is the Boltzmann constant, t is the temperature where the transformation is taking place from liquid to solid.

And also this D is related to k t. So, from here we get del G D since we know viscosity relation with temperature in case of melting. So, viscosity relation with temperature can be related in the form of VFT equation Vogel Fulcher Tammann equation that can be written in this form. Some constant some value let say, so this can also be found out. And this viscosity varies like this in case of weak liquid, this is T m, it varies like this; in case of strong liquid, it varies like this.

So, this is for strong liquid, this is weak liquid. It means that strong liquid means that its viscosity changes very quickly to a very high value and it reaches to a value of 10 to the power 12 to 13 Pascal's second, where the material can be considered as a glass. The strong liquid means it has got very high tendency to form glass or the thickening of the melt is much better than the than that of the weak liquid. So, these are the and also if we come to gamma SL, now, you see that we are getting to the quantification we can measure D, we can measure del G D, we can measure viscosity and that can be related to this. So, all those measurements can be possible in order to find out V.

As well as in case of I, if I consider I, in this I, this can be measured. But when I come to see this part I would see that there are two parameters which are to be measured. In one case which is del G V, del G V can also be usually found out. We can find out V m of a particular metal let say single component system we can also find out del from DSC which is differential scanning calorimetry; and del t the temperature where we would like to take the liquid metal for solidification.

And if I come to this part which is gamma SL, which is little tricky to find out, but experimentally this also can be found out by doing controlled under cooling experiment. Here what we will do you break the metal into small droplets. In order to make sure that one droplet contains one nucleating set, and then we take it to different temperatures and try to see what is the rate at which this number of nuclei is appearing and from that we can get to know gamma SL as well as there could be empirical formula. For example, gamma SL generally it is related to 0.45 to 0.5 of delta by n 0, n 0 is the Avogadro number. So, we can get gamma SL also from this empirical formula. So, we know of every bit of it.

And then simply by considering if I consider this equation, if I consider last class we have seen that if we consider constant nucleation rate and the product which is pure spherical product that product grows at all direction to grows to all the directions at a same rate. Then we get an expression, which is equal to 1 minus exponential minus pi by 3 I V cube t 4. So, this expression we can get where I is constant, V is constant, and 3D growth. So, here if I put I value V value after finding things from here, then we can definitely get any plot which is temperature time. This is my melting T m and this is if, this is my start of the transformation this can be my end of transformation, and somewhere we have T g. And these T g is coming from this plot, which is the viscosity as a function of temperature.

Now, this TTT diagram if I see if I quench, if I take any made like this without touching this line to this point, I can get glass. And if I go along like this or like this, for example, in this case, I would get there are different fraction lines let say this is 1 percent, this is 20 percent, this is 40 percent and this is 99 percent. I see that if I follow this track, then I see that it is not touching 40 percent line, so that means, the maximum amount of crystal that would form in the metal in that melt is around less than 30, less than 40 percent. I can say this is close to 30 percent and rest of the metal would again reach to T g it will form glass.

So, like that way I can have different fraction of crystalline material in a melt or in a glassy matrix. So, then so that decides my temperature time, cooling rate all those information, but actually this cooling rate superimposed on a TTT diagram is not fundamentally right, because these diagrams have been plotted on the basis of isothermal transformation.

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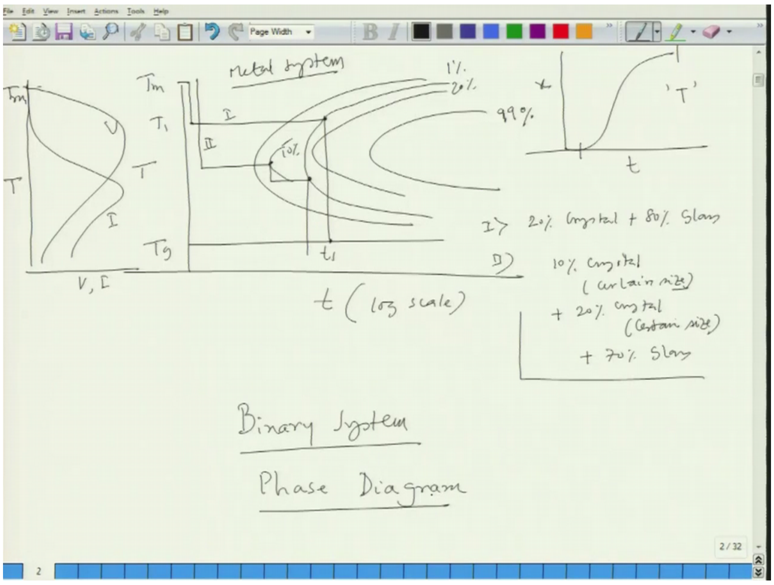

So, actually this thing should have been better if we have a heat treatment practice like this for example, this is my TTT diagram, this is 1 percent, this is 99 percent, this is temperature this is time of course, this is in log scale. So that time I should have this is my T m, I should have done my practice like this. This is my T g. So, I quench it to T 1 let say this line is touching 20 percent line. So, now, I quench it to T 1 hold it for this much of time and then quench it.

And remember during quench it, even if it is touching some other line that should not be considered because during quenching, you are not allowing any atom transfer or atom migration; that means, you are not allowing time to time for those liquid atoms to rearrange themselves to form a extra nucleating sites and subsequent growth. So, now 20 percent crystal will form and then rest of the metal will become glass. So, the composition the fraction would be 20 percent crystal plus 80 percent glass. And once the metal touches T g line, it will form glass.

So, like that another heat treatment cycle I can constitute, I can quench it to this point I can take it to this. Let say this point this is another axis, which is 10 percent. I can take it down, I can heat it there and then quench it. So, now, I can have 10 percent crystal of certain size then I can have 20 percent crystal of certain size and then rest of them will be my metallic glass or the glass, because it is I am considering metal system. If it is a polymer, the situation would be the similar, but that would be polymeric crystal and polymeric glass.

So, like that I can have for example, in this second case, this is first case, second case I can have 10 percent crystal of certain size plus 20 percent crystal of certain size plus 70 percent the glass. And why I am saying certain size because if I try to plot this is U, V and I plot, this is temperature this is time T m. So, growth rate and nucleation rate, this is I, this is V, they are varying like this. So, depending on how many number of nucleus that are available for growth as well as what is the growth rate that would decide what would be the size of that crystal.

So, like that way we can design many other heat treatment routes, but these are this is appropriate because these diagrams have been plotted as in the last class we have seen x with time at a particular temperature. So, these is basically isothermal S curve. So, from that this diagram can also be constituted by projecting those points those points as we have seen in our last lecture. So, this is a better way of representation, because we are not considering continuous cooling rather we are considering a rapid direct quenching to the temperature where transformation is to be taken place and then isothermal holding and then again quenching.

So, no time we are doing continuous cooling at a particular rate. So, this is about if I go back to this particular slide, this is about measurement of those parameters; in case of single component system it is relatively easy. But once we go to multi component system and mainly we will consider binary system, we have to get into little complexity and those complexities will be in the form of how binary phase binary phases evolve. And when we try to see how the binary phases evolve, we have to get into one particular fundamental aspect which is phase diagram.

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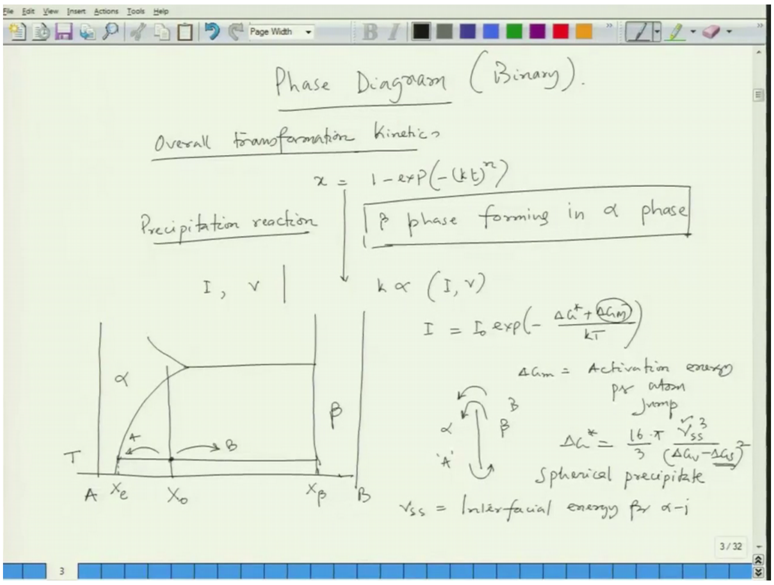

Phase Diagram (Binary).

Overall transformation Kinetics

$x = 1 - \exp(-(kt)^n)$

Precipitation reaction

β phase forming in α phase

I, v

$k \propto (I, v)$

$I = I_0 \exp\left(-\frac{\Delta G^* + \boxed{\Delta G_m}}{kT}\right)$

ΔG_m = Activation energy per atom jump

$\Delta G^* = \frac{16 \cdot \pi}{3} \frac{\gamma_{ss}^3}{(\Delta G_v - \Delta G_s)^2}$

Spherical precipitate

γ_{ss} = Interfacial energy for α-i

Now, let us concentrate on phase diagram, because we will be concentrating more concentrating more on the alloy systems and that to binary systems, let us get into phase diagram. And while we talk about phase diagram, in case of binary, we have to see why it is important, we have been saying that it is important, but why it is important. Now, in last phase, you might have seen that one treatment overall kinetics, we again talked about this general expression. And we have handled one precipitation reaction, where beta phase forming in alpha phase; and in that case, again we try to find out I and V, because in this equation again k is a function of I and V.

But since it is a binary, because we talked about a binary phase diagram, and there we refer this phase diagram with the phase diagram look like this. It is a hypothetical phase diagram where this is alpha phase this is beta phase. And if I try to see a composition where from we are starting this is my x 0, and if I try to see the transformation at this temperature where this is my x e composition and this composition is x beta composition. So, in this phase diagram, we try to find out I, which is again a general expression is like this. And in this case, we have not denoted this as D rather we have denoted it as m delta G m which is nothing but activation energy per atom jump.

In this case, there are two aspects. One is if I have let say alpha and beta interface, those atoms are jumping a alpha phase. Another important aspect what I would like to mention which is A reach and B reach; if the phase becomes b reach that time we term, it as beta and if the phase becomes a reach then we term it as a alpha phase. And alpha is a solid solution if we consider that it is a solid phase reaction then alpha is a solid solution of B in A and A and B are the elements. And beta is another phase which can be a solid solution or a compound that can be decided by the interaction between A and B. So, now this is the situation what we have. So, then we can have A atom going to B side or B atom going to A side depending on where we are. For example, if I quench it to this point then A atom would try to go preferably to this point, and B atom would try to go preferably to this point. So, this is B, and this is A atom, so two phases would form one side would be A reach one side would be B reach.

So, now, in this case, we can have individual atom jump A and A, or since it is a two phase region and the composition distribution has to take place. So, we have also the composition rearrangement rather which is B atom has to go to one side and A atom has to go to another side. So, that time we consider that this particular term is related to the diffusional activation energy for one of those atoms. And del G star again it is related to square. And remember we are talking about spherical precipitate.

And interestingly here we have few other terms one is delta G s, and this is also this is gamma S S, which is the interfacial energy for alpha beta interface. And delta G S is a strain energy. Strain energy, because whenever we have a solid, the another solid when it forms, if that solid crystal structure has got a different crystal structure or its crystal lattice has got a higher lattice parameter or lower lattice parameter than the paired and phase then we would lead to have some sort of straining across the interface between alpha and beta. And that strain energy is dictated in this delta G s, which is a positive term.

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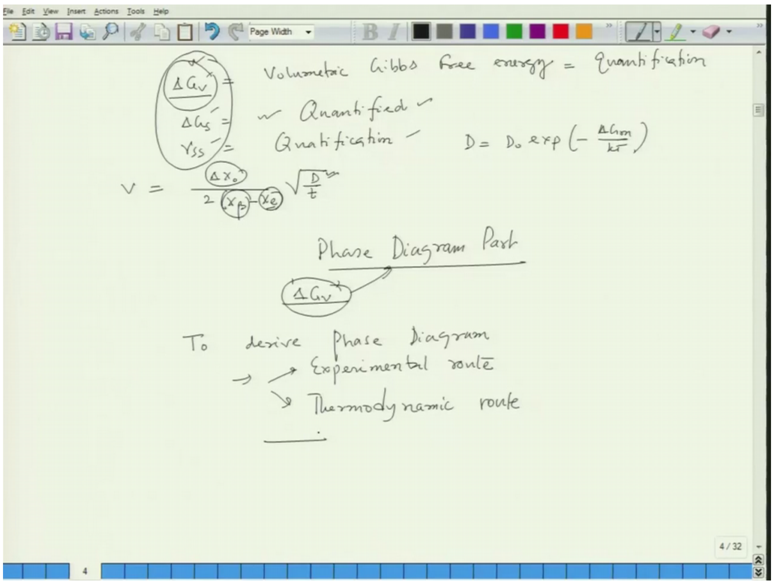

ΔG_v = Volumetric Gibbs free energy = Quantification

ΔG_s = Quantified

γ_{ss} = Quatification

$D = D_0 \exp\left(-\frac{\Delta G_m}{kT}\right)$

$$V = \frac{\Delta x_0}{2(x_\beta - x_e)}\sqrt{\frac{D}{t}}$$

Phase Diagram Part

ΔG_v

To derive Phase Diagram

→ Experimental route

→ Thermodynamic route

And delta G V is nothing but again volumetric Gibbs free energy. So, we have to measure this value, we have to measure this value as well as we have to measure this value. Now, interestingly in this case it is not that straightforward the way we have done for single component system, because in this case we are also coming across compositional variation that is what a treatment to find out this particular value is critical, and is related to phase diagram again rather the way phase diagram is derived.

Similarly, delta G s which is also important and it is to be found out from the matching between lattices of parent and product phase. We have to also quantified; it is to be quantified. And then gamma S S is also an important aspect which can also be found out experimentally, again it is quantification. So, now, this term is to be found out quantification. This is to be quantified, this is also needs to be quantified. If we quantify all those then we can simply get what is the I.

Now, coming to V expression, V is related to delta x 0 divided by 2 x b minus x e root over D by t. Now, delta x 0 is nothing but this. And D is nothing but the diffusivity which is related to D 0 exponential minus delta G m by k T. And this diffusivity we are considering since this alloy is a reach side and we have what we have done we have just taken it to single phase region solutionized it and then quenched it. So, actually your structure is alpha, and then when we have left it here, the alpha phase would like to go to this point because this is the equilibrium alpha composition at temperature T.

So, the rest of the solute which are extra in this particular composition, they will be repelled by the system and then they will from beta of this composition. So, these D is basically nothing but the diffusivity of B in that particular system. X e is the equilibrium composition of alpha solute solution; and x beta is the equilibrium composition of beta phase. So, these can be found out easily from phase diagram. Again we have to see how the phase diagram evolves and D also can be found out experimentally.

So, if we see that our main interest to get into the quantification of heat treatment rather than simply noting that for example, people say heat treatment was tempering, you go to the austenitizing temperature, hold it there, quench it to a temperature below the nose point and hold it there for certain time and then quench it. Now, my question is why should we do that, we have to see the fundamentals behind it, we have to quantify this entire heat treatment practice, so that is what our interest is to go is more on the quantification of different parameters.

So, if I quantify D, if I quantify this, this as well as this, then we can get all the knowledge about this I as well as V and we can get to this point and from that we can easily draw TTT diagram again fine. We will definitely get into the system where how come a TTT diagram can be converted to a CCT diagram, but that will come later on, but first let us concentrate on how we can quantify these factors, these parameters.

So, let us get into first the phase diagram part, which will give information about delta G v. So, we have to quantify this value and for that reason we have to get to the phase diagram. And our interest would be to derive phase diagram, mainly the process by which we can derive phase diagram, one is experimental route, another one is thermodynamic route.

So, in the next lecture we will get into the phase diagram derivation of phase diagram through experimental as well as thermodynamic routes. Let us stop here.

Thank you.